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## PECULIARITIES OF $\gamma$ -INDUCED OPTICAL EFFECTS IN TERNARY SYSTEMS OF AMORPHOUS CHALCOGENIDE SEMICONDUCTORS

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Changes of optical transmittance induced by the influence of  $^{60}\text{Co}$   $\gamma$ -irradiation have been studied in ternary As-Ge-S, Sb-Ge-S, As-Ge-Se and As-Bi-Se systems. The characters of radiation-induced optical effects in all these systems have been compared. It was shown that the compositional dependencies of such effects are almost linear for stoichiometric glasses and reveal some peculiarities connected with phase features, the "free volume" parameters and the specificity of radiation induced defects formation for non-stoichiometric families.

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**Keywords:** Chalcogenide glasses,  $\gamma$ -irradiation, Optical transmittance, Defect formation

### 1. Introduction

Recent investigations of gamma-induced optical phenomena in various ternary systems of amorphous chalcogenide semiconductors (AChS) have shown that the value and character of these induced effects as well as their dynamic and static components essentially depends on the origin, concentration and valency of constituent atoms, the dimensionality, compactness and stoichiometry of structure as well as the concentration of homo- and heteropolar bonds [1-6]. The aim of this work is the comparative analysis of radiation-induced optical effects (RIOE) in different types of AChS systems.

### 2. Experimental

Traditional melt quenching method was used for the preparation of bulk AChS samples of As-Ge-S, Sb-Ge-S, As-Ge-Se and As-Bi-Se systems. 5N purity elements were chosen as precursors for synthesis. The cooled ampoules additionally heated at the temperatures just below the glass transition point  $T_g$  with the aim to avoid the postsynthesis residual stresses.

All samples were irradiated with 1.0-4.4 MGy doses in the conditions of stationary radiation field created in the closed cylindrical capacity by the concentrically placed  $^{60}\text{Co}$  sources. The mean energy of  $\gamma$ -flow was 1.25 MeV; the power of exposure dose was 20 Gy/s. The value of absorbed dose was limited by the unwanted thermoradiation effects, which might suppress RIOE. In our case the temperature in the cavity of radiation sources did not exceed 320-330 K.

Optical transmittance spectra were measured before and after  $\gamma$ -irradiation for a wide range of chemical compositions inside of each system using "Specord M40" spectrophotometer with accuracy 0.5 %. Compositional dependencies of maximal radiation-induced changes of optical transmittance ( $\Delta\tau_{\max}$ ) at the region of fundamental absorption edge (Urbach tail) were chosen as controlled parameters for RIOE investigations.

Taking into account that the RIOE magnitude essentially increases with the sample thickness, obtained glasses were cut into the disks of 0.7-2 mm thickness in dependence on the sensitivity of AChS systems to the influence of  $\gamma$ -irradiation.

In order to analyse the interrelation between RIOE and structural parameters the compactness  $\delta$  was calculated for each composition using known formula [7-12]:

$$\delta = \frac{\sum V_i - V_{\text{exp}}}{V_{\text{exp}}} = \frac{\sum \frac{A_i x_i}{\rho_i} - \sum \frac{A_i x_i}{\rho}}{\sum \frac{A_i x_i}{\rho}}, \quad (1)$$

where  $V_i$  is the volume occupied by the atoms of  $i$ -th chemical element of glass;  $V_{\text{exp}}$  is the experimentally measured volume of glass;  $A_i$ ,  $x_i$  and  $\rho_i$  are the atomic weight, the atomic fraction and the atomic density of  $i$ -th chemical element, respectively;  $\rho$  is the measured density of glass. The quantities  $\delta$  can take the negative values, corresponding to larger "free" volume.

### 3. Results and discussion

#### 3.1. As-Ge-S system

The compositional dependencies of maximum value of optical transmittance difference before and after  $\gamma$ -irradiation for stoichiometric  $\text{As}_2\text{S}_3\text{-GeS}_2$  and non-stoichiometric  $\text{As}_2\text{S}_3\text{-Ge}_2\text{S}_3$  sections of As-Ge-S system are presented in Figs. 1 and 2, respectively. Radiation-induced changes were measured 1 day after irradiation (total RIOE described by  $\Delta\tau_{\text{max}}^{\Sigma}$ ) and 2 months later (static component of RIOE described by  $\Delta\tau_{\text{max}}^{\text{st}}$ ). It is clear that dynamic component of RIOE is equal to the difference between the total effect and static component. The average coordination number  $Z$  (calculated as the number of covalent chemical bonds per atom of the formula unit [13,14]) was chosen as composition parameter. This parameter is appropriate for consideration only in the ternary glasses of  $\text{A}^{\text{IV}}\text{-B}^{\text{V}}\text{-C}^{\text{VI}}$  type when  $Z$  changes essentially with composition.

It must be mentioned that phenomenological model for RIOE in stoichiometric glass compositions can be built on the basis of radiation-induced redistribution of chemical bonds too. Moreover, such processes are confirmed by IR investigations in 400-100  $\text{cm}^{-1}$  region.

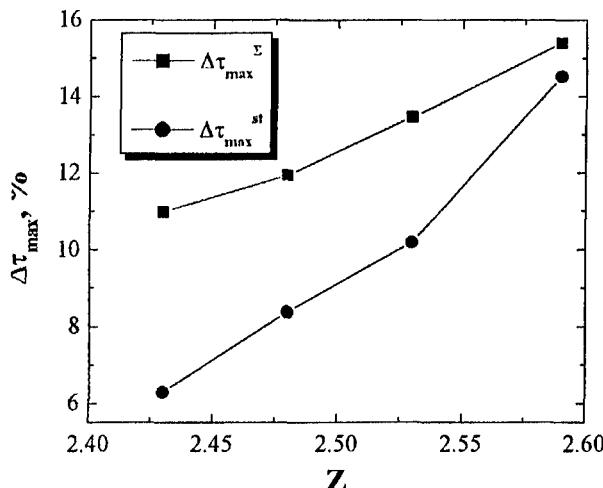


Fig. 1. Dependence of quantitative parameters of total ( $\Delta\tau_{\text{max}}^{\Sigma}$ ) and static ( $\Delta\tau_{\text{max}}^{\text{st}}$ ) RIOE for stoichiometric  $\text{As}_2\text{S}_3\text{-GeS}_2$  section of As-Ge-S system on the average coordination number  $Z$ .

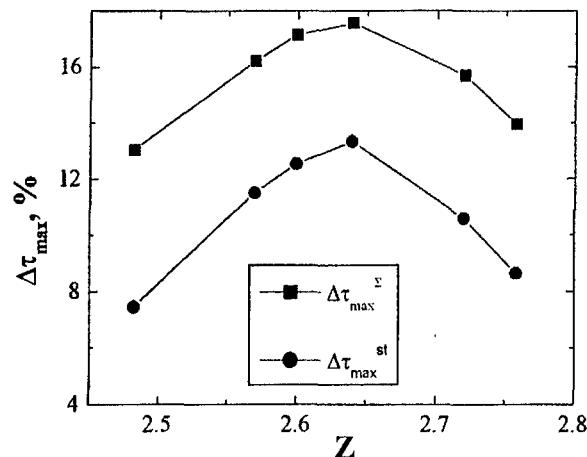


Fig. 2. Dependence of quantitative parameters of total ( $\Delta\tau_{\text{max}}^{\Sigma}$ ) and static ( $\Delta\tau_{\text{max}}^{\text{st}}$ ) RIOE for non-stoichiometric  $\text{As}_2\text{S}_3\text{-Ge}_2\text{S}_3$  section of As-Ge-S system on the average coordination number  $Z$ .

As expected, the linear increasing of  $\Delta\tau_{\text{max}}$  with  $Z$  is observed for stoichiometric compositions. Higher sensitivity of Ge-enriched glasses to  $\gamma$ -irradiation is well explained by the corresponding decreasing of compactness  $\delta$  (see Fig. 3). It can be assumed that radiation-induced defects become stabilize easier inside of the voids (at the increasing of "free" volume) in comparison with more compact structure when the nearness of other atoms promotes the quick healing of these defects.

Calculations of  $\delta$  for non-stoichiometric compositions revealed the minimum value for this parameter at  $Z \approx 2.7$  (Fig. 4 [11]). Such feature agrees with the behaviour of  $\Delta\tau_{\text{max}}^{\Sigma}(Z)$  and  $\Delta\tau_{\text{max}}^{\text{st}}(Z)$  dependencies which demonstrate the maximum RIOE at this point. In the case under consideration the

joint contribution of compactness and bonds concentration into the mechanism of RIOE must be taken into account using the parameter  $\omega$  [7]:

$$\omega = C\delta, \quad (2)$$

where  $C$ - concentration of main chemical bonds, which take part in the radiation-induced defects formation.

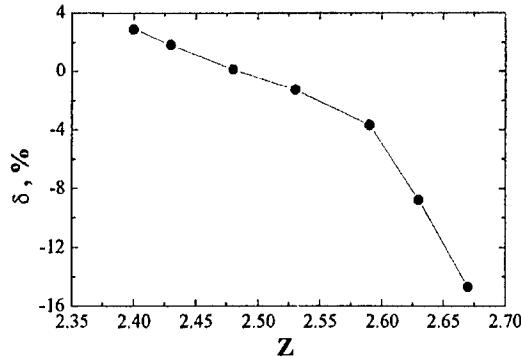


Fig. 3. Dependence of atomic compactness  $\delta$  on average coordination number  $Z$  for  $\text{As}_2\text{S}_3\text{-GeS}_2$  stoichiometric section.

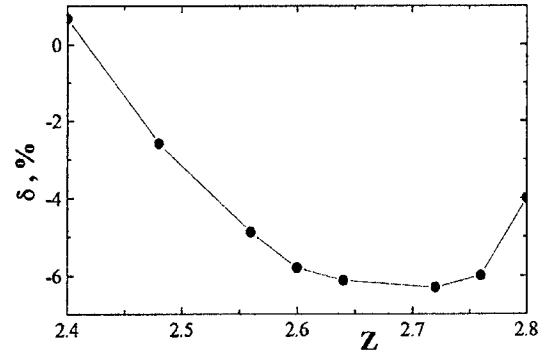


Fig. 4. Dependence of atomic compactness  $\delta$  on average coordination number  $Z$  for  $\text{As}_2\text{S}_3\text{-Ge}_2\text{S}_3$  non-stoichiometric section [11].

### 3.2. Sb-Ge-S system

One more representative of  $\text{A}^{\text{IV}}\text{-B}^{\text{V}}\text{-C}^{\text{VI}}$  type ternary systems is Sb-Ge-S. The  $\Delta\tau_{\max}(Z)$  dependencies of total RIOE and its static component for stoichiometric  $\text{Sb}_2\text{S}_3\text{-GeS}_2$  and non-stoichiometric  $\text{Sb}_2\text{S}_3\text{-Ge}_2\text{S}_3$  sections are presented in Fig. 5 and Fig. 6, respectively. In both cases Sb-enriched samples do not reveal any RIOE. This is connected with the nature of Sb atoms, which exhibit exceptional ability to the passivation of RIOE by the preventing of radiation-induced defects stabilization. Such ability is associated with the high level of metallization in Sb-containing chemical bonds and the high compactness of these glasses. The  $\delta(Z)$  curve has a similar shape as in the case of As-Ge-S. As the consequence, for this non-stoichiometric section, in contrast to  $\text{As}_2\text{S}_3\text{-Ge}_2\text{S}_3$ , the characters of  $\Delta\tau_{\max}(Z)$  and  $\delta(Z)$  dependencies mismatch.

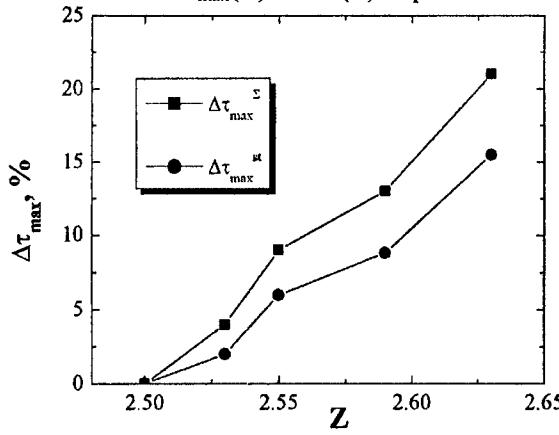


Fig. 5. Dependence of quantitative parameters of total ( $\Delta\tau_{\max}^{\Sigma}$ ) and static ( $\Delta\tau_{\max}^{\text{st}}$ ) RIOE for stoichiometric  $\text{Sb}_2\text{S}_3\text{-GeS}_2$  section of Sb-Ge-S system on the average coordination number  $Z$ .

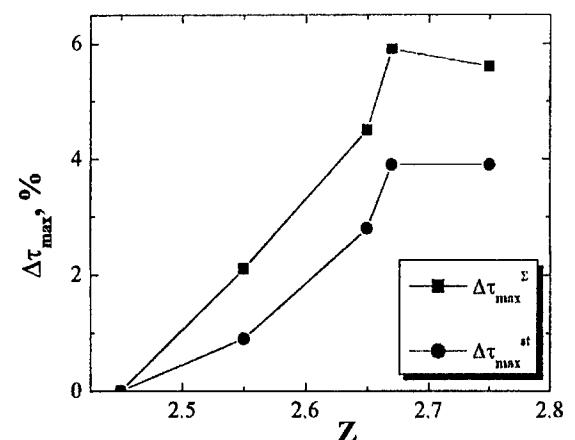


Fig. 6. Dependence of quantitative parameters of total ( $\Delta\tau_{\max}^{\Sigma}$ ) and static ( $\Delta\tau_{\max}^{\text{st}}$ ) RIOE for non-stoichiometric  $\text{Sb}_2\text{S}_3\text{-Ge}_2\text{S}_3$  section of Sb-Ge-S system on the average coordination number  $Z$ .

### 3.3 As-Ge-Se system

In order to analyse the features of RIOE in the whole range of  $Z$  variation the  $\gamma$ -induced changes of optical transmittance in  $\text{As}_x\text{Ge}_y\text{Se}_{1-x-y}$  system was studied. Extremum points can be observed at  $Z \approx 2.4$  and  $Z \approx 2.7$ . First point undoubtedly represents the well-known rigidity transition

[15,16]. Second point is the subject of discussions up and it is often attributed to 2D-3D topological phase transition [13] or to the phase separations [17].

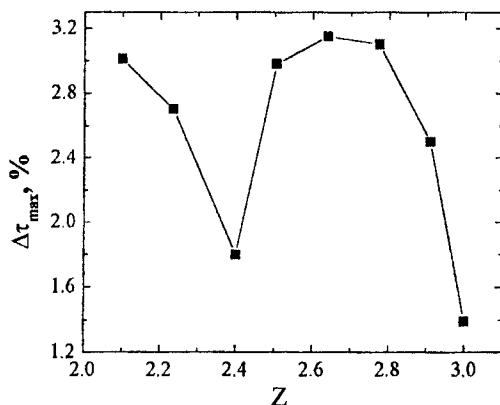


Fig. 7. Dependence of maximal radiation-induced change of transmittance on the average coordination number  $Z$  for non-stoichiometric  $\text{As}_x\text{Ge}_y\text{Se}_{1-x-y}$  family of As-Ge-Se system.

### 3.3. As-Bi-Se system

Sometimes even small quantities of additions cause the essential radiation-induced changes of optical transmittance. One of such examples is the chemical modification of stoichiometric  $\text{As}_2\text{Se}_3$  by Bi. Maximal RIOE takes place when the Bi concentration is  $\sim 0.5$  at. % (Fig. 8) and, as it is assumed, the concentration of  $(\text{Bi}_2^-, \text{Se}_3^+)$  and  $(\text{Bi}_4^+, \text{Se}_1^-)$  defect pairs is highest.

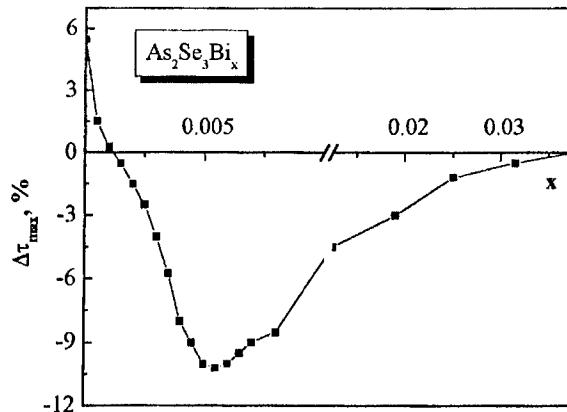


Fig. 8. Dependence of maximal radiation-induced change of transmittance on the content of Bi for stoichiometric  $\text{As}_2\text{Se}_3$  chemically modified by Bi.

Taking into account that in some glasses addition of Bi can change the type of electrical conduction, it is important to clear the mechanism of Bi entering of into the glass matrix. The most popular explanations are the change of Bi coordination in dependence on its concentration and the increasing of disequilibrium between the concentrations of positively and negatively charged defects [19]. So, the mechanism of RIOE in  $\text{As}_2\text{Se}_3\text{Bi}_x$  glasses is intricate problem and needs an additional detail studies.

## 4. Conclusions

Investigations of  $\gamma$ -induced changes of optical transmittance show that mechanism of RIOE consists in the coordination defects formation under the radiation treatment. The peculiarities of this process are determined by structural features of glass, its composition, stoichiometry, parameters of

free volume, concentration of main chemical bonds as well as by the origin of constituent chemical elements.

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